

# The Synthesis, Characterization, and Systematic Fire Safety Evaluation of High Volume and Specialty Hydrolytically Stable Phosphine Oxide Containing Polymeric Materials

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**Introduction:** The research is attempting to determine whether or not chemically incorporated hydrolytically stable phosphorus systems can produce major improvements in fundamental fire resistant behavior. This chemically incorporated approach contrasts with the normal industrial method of physically adding fire retardants to the material systems. The disadvantage of the current approach includes the ideas that mechanical properties are impaired by the physical additives. Secondly, the additives may be extractable under conditions of use, possibly even producing unattractive, toxic byproducts. In contrast, the chemically incorporated systems will not be extracted by detergents or subjected to environmental degradation by normal humidity in the air. Preliminary small scale burning tests and dynamic thermogravimetric analysis methods have been very encouraging. The NIST project is the first effort achieving a more fundamental understanding through the use of cone calorimetry methodologies, which permit determination of heat release rate, heats of combustion, smoke generation, and carbon monoxide generation.

**Experimental and Discussion:** During the past year it has been possible to synthesize a number of triphenyl phosphine oxide containing monomers, including the diamine, the dicarboxylic acid, the bisphenol, and the diglycidyl ether, and to use these monomers to prepare polyesters, polyamides, polycarbonates, and to generate epoxide networks. The structures of the most utilized monomers are provided below.

Polyamides have been generated which contained 10, 20, and 30 weight percent of the corresponding triphenyl phosphine oxide dicarboxylic acid. The interest here was the possibility of making a semicrystalline high volume fiber forming material which would show inherent flame resistance. Briefly, the heat release rate and heat of combustion were definitely decreased by the introduction of the phosphine oxide comonomer (Figure 1). Polycarbonates are also high volume engineering thermoplastics and it was of great interest to investigate whether the phosphine oxide bisphenol could be synthesized and copolymerized with the high volume bisphenol-A component. The initial results on copolymerization of the phosphine oxide bisphenol with bisphenol-A under commercial polycarbonate synthesis conditions have been quite promising. Tough, ductile, transparent materials have been obtained which are compression moldable. An increase in char yield as a function of phosphine oxide bisphenol has been realized. These samples are currently being prepared for evaluation by cone calorimetry. The efforts in these two areas are more thoroughly summarized in two papers which have been prepared for presentation at the American Chemical Society meeting on fire resistant materials in August of this year.

Epoxy diamine cured networks have also been investigated (Figure 2, Figure 3, and Table 1). These systems are more or less the backbone of aerospace matrix resin materials and fire resistance improvement is of great interest for aircraft interiors and also for marine applications. The characteristics of 30 mol percent BAPPO cured Epon resins were evaluated by an initial study by cone calorimetry. The resulting networks, even with only 30 percent of the curing agent containing phosphorus, were moderately encouraging and heat and combustion reduction for this system was demonstrated.

At this point it has been demonstrated that the phosphorus containing materials show a significantly higher char yield than their non-phosphorus conventional counterparts, as shown in Figure 3 below. Other phosphorus containing monomers with an increased concentration of phosphorus are being investigated in order to determine whether the increased phosphorus content and decreased aromatic structure will improve both heat release rate and at the same time diminish carbon monoxide generation.

**Acknowledgments:** This research was supported by the National Institute of Standards and Technology, Grant No. 70NANB3H1434, with T. Kashiwagi of the Building and Fire Research Laboratory serving as Scientific Officer.

## References

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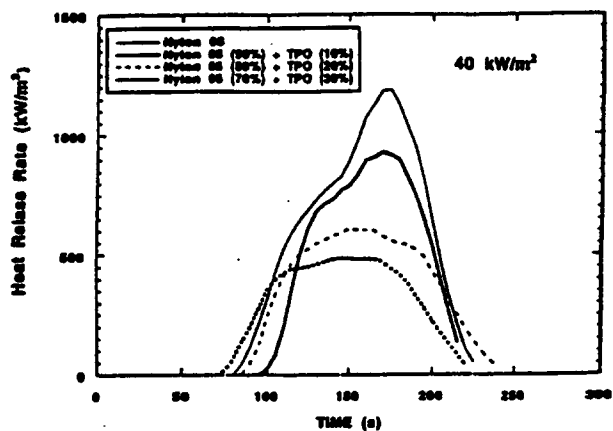


Figure 1: Heat Release Rate of Triaryl Phosphine Oxide Containing Nylon 6,6, Copolymers

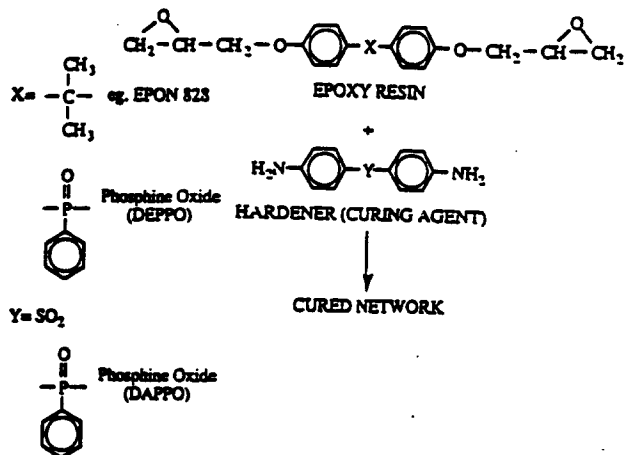


Figure 2: Development of Fire Resistant Cured Epoxy Networks Matrix and Adhesive Materials

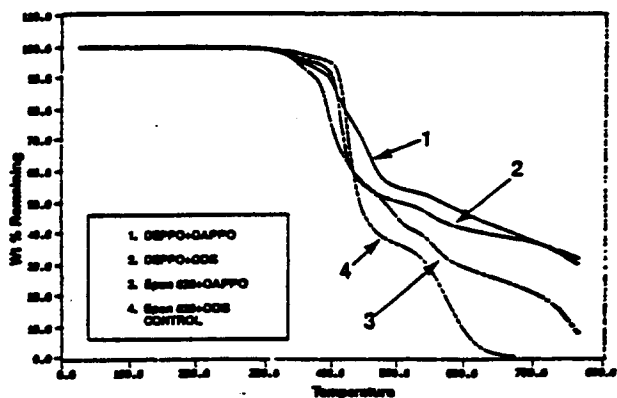


Figure 3: High Char Yields are Generated when New Epoxy Polymers are Degraded in Air

Epoxy Sample	Weight Remained		
	at 600°C	at 700°C	at 760°C
EPON 828-DDS	8.4%	0%	0%
EPON 828-DAPPO	29.0%	20.6%	8.25%
EPON 828-DAMPO	34.9%	26.1%	20.3%
EPON 828-BAPPO	37.5%	29.2%	21.6%
EPON 828-BAMPO	47.3%	38.6%	31.8%

Table 1: Thermal Stability of Epoxy Polymers 1